

## THERMOPLASTIC POLYMER ADDITIVE COMPOSITIONS

This invention relates to thermoplastic polymer additive compositions and their  
5 use. In particular it relates to such additive compositions that are useful as  
colour stabilisers for thermoplastic moulding compositions and thermoplastic  
materials, especially when such materials are recycled.

Polyethylene terephthalate is widely employed in the manufacture of  
10 packaging items. One large application for polyethylene terephthalate is in the  
manufacture of food packaging items and, in particular, beverage bottles.  
Such beverage bottles are extensively utilised for carbonated soft drinks and  
are increasingly more attractive, for safety considerations, in the packaging of  
alcoholic beverages such as beer. Bottles used for still or carbonated water or  
15 other soft drinks are typically colourless, green or blue. However, this  
invention is particularly, although not exclusively, concerned with colourless  
and near-colourless bottles.

Other uses for polyethylene terephthalate moulding compositions include the  
20 manufacture of packages for agrochemicals, cosmetics, detergents and the  
like.

Polyethylene terephthalate bottles are usually manufactured using a two stage  
process. Granules of the polyethylene terephthalate, along with any relevant  
25 additives, are injection moulded in a first step to produce a preform. The

resulting preform is then blow moulded, possibly at a different factory, in a second step to the desired shape. Machines are also available which make bottle preforms and then blow them immediately into bottles.

- 5 Typical temperatures required for injection moulding of polyethylene terephthalate moulding compositions are between about 260°C and about 285°C or higher, e.g. up to about 310°C. Somewhat lower temperatures in excess of about 100°C up to about 170°C or more are generally used in the blow-moulding step to produce a bottle from a polyethylene terephthalate
- 10 preform.

It is a recognised phenomenon within the industry that use of extended dwell times at elevated temperatures, particularly during the injection moulding step used to make a polyethylene terephthalate bottle preform but also possibly

15 during the subsequent blow moulding step, may tend to result in an inferior colouration of the preform or blow moulded bottle, in particular by yellowing of colourless materials, and/or inferior light transmission (e.g. haze, clearness or clarity) properties.

- 20 It is further recognised that, with an increase in usage of polyethylene terephthalate and other thermoplastic materials for manufacture of packaging and other articles, a greater need arises to address the problem of disposal of the waste material. With land fill space becoming evermore scarce and with society being generally more environmentally aware than ever before, there is
- 25 an increasing demand that the recycling option be taken. A limited amount of

recycled polyethylene terephthalate material is already employed to produce strapping for packaging. Recycled polyethylene terephthalate is also used in the fibre industry to provide such products as wadding and sound insulation for cars and carpets. However, a more satisfactory option would be to recycle

5 colourless or substantially colourless packaging of a sufficient quality such that it may be reused for food or drink applications. Presently, colourless polyethylene terephthalate material may be recycled or reused either with or without the addition of colouring. However, the recycling of colourless polyethylene terephthalate can give rise to a yellowing of the recycled material.

10 The light transmission properties (e.g. haze, clearness or clarity) of the recycled material may also be unsatisfactory compared to the original material.

Other thermoplastic materials that are in widespread use include polyolefins, such as polyethylene and polypropylene, and polyvinyl chloride. However, this

15 invention is concerned only with polyethylene terephthalate.

It would be desirable to be able to recycle previously used colourless or substantially colourless polyethylene terephthalate in order to produce a material whose colour would permit it to be recycled for further use, for

20 example as a recycled, colourless or substantially colourless, polyethylene terephthalate bottle.

There is a need to provide a thermoplastic polymer additive composition for incorporation into polyethylene terephthalate moulding compositions that will

25 stabilise the colour of the polyethylene terephthalate on injection moulding

and/or on recycling. There is a further need to provide a substantially colourless polyethylene terephthalate moulding composition that, after having been formed into bottles or other moulded articles, is suitable for recycling to make further bottles or other articles of a commercially acceptable colour.

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There is a further need to provide colourless or substantially colourless blow moulded articles, such as bottles, and colourless or substantially colourless preforms therefor, which exhibit good gas barrier properties and which provide protection for the contents against ultra-violet light, and which have a good recycling potential.

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It is an object of the present invention to provide recycling potential to colourless articles made from polyethylene terephthalate where that has not been possible or desirable previously due to restrictions placed upon the utility of the recycled material as a result of its colour and/or light transmission properties.

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According to a first aspect of the present invention there is provided a thermoplastic polymer additive composition for addition to a thermoplastic moulding composition, said additive composition comprising at least one hindered amine light stabiliser and at least one acetaldehyde scavenger.

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Preferably, the additive composition is such that when it is added to a moulding composition (and a 2.5mm thick plaque is made as described in Example 1 hereinafter), the % transmission at 450nm and/or 550nm of the moulding

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composition which includes the additive composition (e.g. the plaque) is greater than the % transmission measured in an identical manner on an identical material (e.g. plaque) except that such material does not include a hindered amine light stabiliser.

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It is postulated that the deleterious effects on light transmission and/or on colour properties of polyethylene terephthalate moulded articles apparently caused by acetaldehyde scavengers can be mitigated by the inclusion in the melt of a hindered amine light stabiliser. Accordingly, in a second aspect, the present invention provides the use of a hindered amine light stabiliser as an additive in a polyethylene terephthalate moulding composition comprising an acetaldehyde scavenger to reduce discolouration and/or haze and/or increase the degree of light transmission after moulding of the composition. The moulding composition may be a recyclate, in which case the use of a hindered amine light stabiliser is thought to be particularly effective in reducing discolouration and/or haze, which may occur as a result of solid stating procedures used during recycling.

In a third aspect, the invention extends to a method of increasing the degree of light transmission after moulding of a polyethylene terephthalate moulding composition comprising an acetaldehyde scavenger, the method comprising including a hindered amine light stabiliser as an additive in the moulding composition.

The hindered amine light stabiliser and the acetaldehyde scavenger may be added concurrently to a moulding composition; or hindered amine light stabiliser may be added to a moulding composition which already includes a said acetaldehyde scavenger. In a less preferred embodiment, an  
5 acetaldehyde scavenger may be added to a moulding composition which already includes a hindered amine light stabiliser.

An increase in the degree of light transmission in accordance with the second and third aspects may be confirmed by comparing the % transmission (at  
10 450nm and/or 550nm) after moulding a said moulding composition which includes a said hindered amine light stabiliser as a said additive, to a moulding composition which is equivalent in all respects except that it does not include a said hindered amine light stabiliser.

15 An increase in the degree of light transmission may be confirmed using the procedure set forth in Example 1 hereinafter.

Preferably, inclusion of the hindered amine light stabiliser results in an increase in the degree of light transmission (of for example a plaque) after  
20 moulding across at least 50% (preferably at least 60%, more preferably at least 70%, especially at least 80%) of the wavelength range 400-600nm. An increase as aforesaid will be readily apparent from a plot of % transmission against wavelength, for example as shown in Figures 5 to 7 hereinafter.

It has been found that hindered amine light stabilisers are capable of acting synergistically with acetaldehyde scavengers to reduce acetaldehyde content. Accordingly, in a fourth aspect, the invention further provides the use of a hindered amine light stabiliser as an additive in a thermoplastic moulding composition comprising polyethylene terephthalate and an acetaldehyde scavenger for, synergistically with the acetaldehyde scavenger, reducing the acetaldehyde content of a moulded article formed from the composition

The thermoplastic polymer additive composition of the invention may be provided in a form suitable for direct addition to a thermoplastic melt or pre-melt granular composition. For example, the thermoplastic polymer additive composition may be uniformly dispersed in an inert liquid carrier therefor.

The thermoplastic moulding composition is preferably one that tolerates or requires high temperature processing conditions, for example use of an injection moulding temperature of at least about 200°C. Suitable materials include polyethylene terephthalate.

In order to mould articles from a thermoplastic moulding composition it is necessary to heat the composition to a temperature above its softening point. However, it is normally preferred to perform moulding at a temperature below the melting point of the thermoplastic polymer material present in the thermoplastic moulding composition. In the practice of the present invention, it will often be preferred to utilise thermoplastic polymer materials in the moulding composition which can tolerate, or which require the use of, high

processing temperatures, for example temperatures of at least about 200°C. Some moulding processes may require the use of more severe processing conditions than others. For example, in the formation of a blow moulded polyethylene terephthalate bottle, injection temperatures in the range of from  
5 about 260°C to about 285°C or more, e.g. up to about 310°C, can be used in the course of forming a bottle preform whereas a lower temperature of, for example, from about 100°C up to about 170°C is typically used, in combination with a suitable high air pressure of, for example, about 40 bar, in order to blow a bottle of the desired shape from the bottle preform.

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Mechanical recycling procedures may involve the following steps:

1. Collection (e.g. of bottles). This is usually organised through bottle collection points and some times by street collection.
2. Colour sorting. This is often done manually although more in-line  
15 automated systems are becoming available. The commercial value of polyethylene terephthalate coloured bottles is: clear > blue > green > amber/other transparent and translucent colours > opaque. Clear, blue and green can be blended to give an acceptable final resin colour. Other colours find use either in strapping and staple fibre. There are also some applications  
20 in crates and pallets. The recycling of colourless or substantially colourless bottles to produce recycled colourless or substantially colourless bottles has been difficult because of the tendency of the recycled materials to yellow and/or become hazy.
3. Grinding. Typically the bottles are ground into fragments of typical  
25 thickness 0.15 to 0.4 mm in size of approximately 1 to 2 cm.



4. Separation of polyethylene terephthalate from contaminants. This is usually done by flotation or other means such as air separation. This removes closures, labels, internal barrier layers, soil etc.
5. Washing. Typical composition of a wash is 1.8% sodium hydroxide.
- 5 Bottles are typically washed at 80° to 85°C. This removes external barrier layers, plus more importantly, microbiological material and potentially toxic compounds.
6. Drying. Usually by hot air.
7. Extrusion and pelletizing. A vacuum pump is employed to remove
- 10 volatiles.
8. Solid stating. This is usually conducted by convected heating and 200°C for 8 to 12 hours, or longer – for example up to about 16 hours or even more. This increases the IV to the required level. For bottle blowing this is typically 0.72 - 0.84 dL/g.

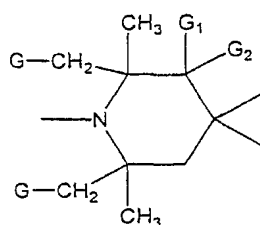
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The solid stating procedure in recycling has tended to cause a yellowing in polyethylene terephthalate materials, particularly in such materials that contain an acetaldehyde scavenger. It has now been discovered that in the recycling of a polyethylene terephthalate material that comprises an acetaldehyde

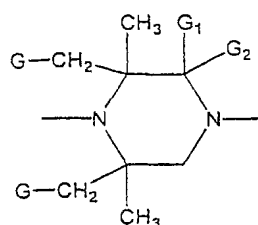
20 scavenger, the addition to the recyclates of a hindered amine light stabiliser before the solid stating step can reduce this problem.

Said hindered amine light stabiliser suitably includes a piperazine or a piperidine moiety. Said hindered amine light stabiliser preferably includes a

25 moiety of formula I or II.



(I)



(II)

wherein

- 5 G is hydrogen, methyl or a linking atom or group and  
 G<sub>1</sub> and G<sub>2</sub> are hydrogen, methyl, a linking atom or group or together are oxygen.

Preferably, G is hydrogen or methyl; and G<sub>1</sub> and G<sub>2</sub> are hydrogen or methyl.

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Hindered amine light stabilisers may be selected from compounds III to XVIII shown in Figures 1 to 4 wherein n and m are integers with m' being in the range 2 to 200 and n suitably being in the range 2 to 5.

- 15 Preferred hindered amine light stabilisers suitable for use in the present invention include: Chimassorb<sup>TM</sup> 944 (CAS No. 71878-19-8), also known as poly[6-[(1,1,3,3-tetramethylbutyl)amino]1,3,5-triazine-2,4-diyl]-[(2,2,6,6-tetramethyl-4-piperidyl)-imino]hexamethylene[(2,2,6,6-tetramethyl-4-piperidyl)imino], Chimassorb<sup>TM</sup> 2020 (CAS No. 192268-64-7), also known as  
 20 poly-[[6-[N-(2,2,6,6-tetramethyl-4-piperidiny)-n-butylamino]-1,3,5-triazine-2,4-diyl][(2,2,6,6-tetramethyl-4-piperidiny)imino]-1,6-hexanediyl[2,2,6,6-

tetramethyl-4-piperidinyloxyimino]]-alpha-[N,N,N',N'-tetrabutyl-N''-(2,2,6,6-tetramethyl-4-piperidinyloxy)-N''-[2,2,6,6-tetramethyl-4-piperidinyloxyamino]-hexyl]-[1,3,5-triazine-2,4,6-triamine]omega-N,N,N',N'-tetrabutyl-1,3,5-triazine-2,4-diamine, Tinuvin<sup>TM</sup> 622 (CAS No.65447-77-0), Tinuvin<sup>TM</sup> 770 (Cas No. 52829-07-9), also known as sebacic acid, bis(2,2,6,6-tetramethyl-4-piperidyl)ester, and Cyasorb<sup>TM</sup> UV3346 (CAS No.082451-48-7), also known as poly(6-morpholino-1,3,5-triazine-2,4,6-triyl)[(2,2,6,6-tetramethyl-4-piperidyl)imino]-hexamethylene-[(2,2,6,6-tetramethyl-4-piperidyl)-imino].

10 Preferred hindered amine light stabilisers include a piperidine moiety. Preferred stabilisers include a moiety I referred to above. In moiety I, preferably each G represents a hydrogen atom and G<sub>1</sub> and G<sub>2</sub> represent hydrogen atoms. Said stabilisers preferably include a -(CH<sub>2</sub>CH<sub>2</sub>)<sub>p</sub>- moiety where p is in the range 1 to 10, preferably 1 to 6. Suitably, they have an average molecular weight (Mn) in the range 300 to 10000, preferably in the range 500 to 7000, more preferably in the range 1000 to 5000, especially in the range 1300 to 4000.

An especially preferred hindered amine light stabiliser is CHIMASSORB 944 (compound VII shown in Figure 2).

Preferred acetaldehyde scavengers include one or more nitrogen atoms. Preferably, the nitrogen atoms are not bonded to other atoms by double or triple bonds, but are preferably bonded to three other atoms by single bonds.

25 Preferred scavengers include amine moieties. Preferred amine moieties are

primary and secondary amine moieties. Especially preferred are scavengers which include a  $\text{-NH}_2$  moiety.

In one embodiment, preferred acetaldehyde scavengers include both amine  
5 moieties as described and amide moieties. In one embodiment, preferred  
acetaldehyde scavengers include a substituted phenyl moiety. In one  
preferred embodiment, a said acetaldehyde scavenger may include an amine  
moiety (especially  $\text{-NH}_2$ ), an amide moiety (especially  $\text{-CONH}_2$ ) and a  
substituted phenyl moiety. In this case, it is preferred that both the amine  
10 moiety and the amide moiety are directly bonded to the phenyl moiety.  
Preferably, the amine moiety and amide moiety are bonded ortho to one  
another.

One class of acetaldehyde scavengers may be as described in US 5340884  
15 (Eastman), the content of which as regards the scavengers is incorporated  
herein by reference. In this case, the scavenger may be a polyamide selected  
from the group consisting of low molecular weight partially aromatic  
polyamides having a number average molecular weight of less than 15,000,  
low molecular weight aliphatic polyamides having a number average molecular  
20 weight of less than 7,000, and combinations thereof. Preferred low molecular  
weight partially aromatic polyamides include: poly(m-xylylene adipamide),  
poly(hexamethylene isophthalamide), poly(hexamethylene adipamide-co-  
isophthalamide), poly(hexamethylene adipamide-co-terephthalamide), and  
poly(hexamethylene isophthalamide-co-terephthalamide). The most preferred  
25 low molecular weight partially aromatic polyamide is poly(m-xylylene

adipamide) having a number average molecular weight of 4,000 to 7,000 and an inherent viscosity of 0.3 to 0.6 dL/g. Preferred low molecular weight aliphatic polyamides include poly(hexamethylene adipamide) and poly(caprolactam). The most preferred low molecular weight aliphatic  
5 polyamide is poly(hexamethylene adipamide) having a number average molecular weight of 3,000 to 6,000 and an inherent viscosity of 0.4 to 0.9 dL/g.

Another class of acetaldehyde scavengers may be as described in US 6762275 (Coca-Cola), the content of which as regards the scavenger is  
10 incorporated herein by reference. In this case, the scavenger may include at least two component molecular fragments, each component molecular fragment comprising at least two hydrogen substituted heteroatoms bonded to carbons of the respective component molecular fragment. The component molecular fragments of the organic additive compound are each reactive with  
15 acetaldehyde in a polyester to form water and a resulting organic molecular fragment comprising an unbridged five or six member ring including the at least two heteroatoms. Preferably, the organic additive compounds have at least twice the molecular weight of the component molecular fragments alone. The heteroatoms present in each molecular fragment capable of reacting with  
20 acetaldehyde include oxygen (O), nitrogen (N), and sulfur (S). The heteroatoms of the component molecular fragments suitably have at least one bond to an active hydrogen (H), and in the course of condensing with acetaldehyde should split off water. Preferred functional groups containing these heteroatoms include amine (NH<sub>2</sub> and NHR), hydroxyl (OH), carboxyl  
25 (CO<sub>2</sub>H), amide (CONH<sub>2</sub> and CONHR), sulfonamide (SO<sub>2</sub>NH<sub>2</sub>), and thiol (SH).

It is necessary for these functional groups to be sterically arranged so that on condensation with AA an unbridged 5 or 6 member ring can be formed. It is preferred that the structural arrangement allows the formation of a six membered ring. It is especially preferred that heteroatoms of the organic additive are attached to a preformed ring or rings. It is most preferred that the preformed ring(s) are aromatic so that the unbridged 5 or 6-member ring of the resulting organic compound is bonded to the aromatic ring. Suitable organic additive compounds may be substantially thermally stable at the temperatures required for melt-processing the polyester. It is also preferred that the functional groups present on the organic additive are relatively unreactive towards the ester linkages present in polyesters. Examples of preferred scavengers include 1,2-bis(2-aminobenzamidoyl)ethane; 1,2-bis(2-aminobenzamidoyl)propane; 1,3-bis(2-aminobenzamidoyl)propane; 1,3-bis(2-aminobenzamidoyl)pentane; 1,5-bis(2-aminobenzamidoyl)hexane; 1,6-bis(2-aminobenzamidoyl)hexane; and 1,2-bis(2-aminobenzamidoyl)cyclohexane. More preferred are scavengers where the component molecular fragments are derived from anthranilamide, because of their low cost, efficacy, and ease of incorporation into PET.

An especially preferred scavenger of said class is 1,6-bis (2-aminobenzamidoyl hexane).

Another group of acetaldehyde scavengers suitable for use in the present invention include Anthranilamide, 1,8-diaminonaphalene, Allantoin, 3,4-diaminobenzoic acid, Malonamide, Salicylanilide, 6-amino-1,3-dimethyluracil

(DMU), 6-Aminoisocytosine, 6-Aminouracil, 6-Amino-1-methyluracil,  $\alpha$ -tocopherol, triglycerin, trimethylolpropane, dipentaerythritol, tripentaerythritol, D-mannitol, D-sorbitol, and xylitol. From the aforementioned group, Anthranilamide, 1,8-diaminonaphthalene, Allantoin, 3,4-diaminobenzoic acid, 5 Malonamide, Salicylanilide, 6-amino-1,3-dimethyluracil (DMU), 6-Aminoisocytosine, 6-Aminouracil, 6-Amino-1-methyluracil are preferred.

Preferably, a said hindered amine light stabiliser is selected from a compound which includes moiety I wherein each of G, G<sub>1</sub> and G<sub>2</sub> represent hydrogen 10 atoms; and a said acetaldehyde scavenger is selected from Anthranilamide, 1,8-diaminonaphthalene, Allantoin, 3,4-diaminobenzoic acid, Malonamide, Salicylanilide, 6-amino-1,3-dimethyluracil (DMU), 6-Aminoisocytosine, 6-Aminouracil, 6-Amino-1-methyluracil, 1,2-bis(2-aminobenzamidoyl)ethane, 1,2-bis(2-aminobenzamidoyl)propane, 1,3-bis(2-aminobenzamidoyl)propane, 1,3-15 bis(2-aminobenzamidoyl)pentane, 1,5-bis(2-aminobenzamidoyl)hexane, 1,6-bis(2-aminobenzamidoyl)hexane and 1,2-bis(2-aminobenzamidoyl)cyclohexane.

Preferably, the thermoplastic moulding composition comprises a polyester, 20 especially polyethylene terephthalate. Polyethylene terephthalate used for injection moulding purposes is typically post-condensed and has a molecular weight in the region of about 25,000 to 30,000. However, it has also been proposed to use a fibre grade polyethylene terephthalate that is cheaper but is non-post-condensed, with a lower molecular weight in the region of about 25 20,000. It has further been suggested to use co-polyethylene terephthalates of

polyethylene terephthalate which contain repeat units from at least 85 mole % terephthalic acid and at least 85 mole % of ethylene glycol. Dicarboxylic acids which can be included, along with terephthalic acid, are exemplified by phthalic acid, isophthalic acid, naphthalene-2,6-dicarboxylic acid, cyclohexanedicarboxylic acid, cyclohexanediacetic acid, diphenyl-4,4'-dicarboxylic acid, succinic acid, glutaric acid, adipic acid, azelaic acid and sebacic acid. Other diols which may be incorporated in the co-polyethylene terephthalates, in addition to ethylene glycol, include diethylene glycol, triethylene glycol, 1,4-cyclohexanedimethanol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol, hexane-1,6-diol, 3-methylpentane-2,4-diol, 2-methylpentane-1,4-diol, 2,2,4-trimethylpentane-1,3-diol, 2-ethylhexane-1,3-diol, 2,2-diethylpropane-1,3-diol, hexane-1,3-diol, 1,4-di(hydroxyethoxy)-benzene, 2,2-bis-(4-hydroxycyclohexyl)-propane, 2,4-dihydroxy-1,1,3,3-tetramethylcyclobutane, 2,2-bis-(3-hydroxyethoxyphenyl)-propane, and 2,2-bis-(4-hydroxypropoxyphenyl)-propane. In this specification the term "polyethylene terephthalate" includes not only polyethylene terephthalate but also such co-polyethylene terephthalates.

Injection moulding of polyethylene terephthalate and other polyethylene terephthalate moulding compositions is typically carried out using an injection moulding machine and a maximum barrel temperature in the range of from about 260°C to about 285 C or more, for example, up to about 310°C. The dwell time at this maximum temperature is typically in the range of from about 15 seconds to about 5 minutes or more, preferably from about 30 seconds to about 2 minutes.



It is well known within the industry that polyethylene terephthalate does not exhibit good gas barrier properties. When producing bottles that will be used to package carbonated drinks or alcoholic beverages it is desirable to prevent carbon dioxide from escaping and being replaced by oxygen. It has accordingly been proposed to add a polyamide to the thermoplastic polyethylene terephthalate moulding composition in order to confer improved gas barrier properties on it. Alternatively a sandwich construction may be used in which nylon or an ethylene/vinyl alcohol resin is incorporated in a multi-layer preform which is then blow moulded to form a bottle having improved gas barrier properties.

The thermoplastic polymer additive of the invention may be added as a solid masterbatch in the form of granules or powder. Alternatively, the additive may be suspended or dissolved in a liquid carrier in order to ensure a uniform dispersion of the additive throughout the polyethylene terephthalate. The liquid carrier is generally an inert material, such as a hydrocarbon oil, an ester, an alcohol, or a mixture of two or more thereof. The liquid carrier is selected to be non-toxic, to have good compatibility with polyethylene terephthalate and to possess good solvent properties (if the additive is to be dissolved in the liquid carrier). Ideally, the quantity of carrier included in the composition is kept to a minimum in order that the properties of the polyethylene terephthalate are not adversely affected. The thermoplastic polymer additive composition of the present invention may include a thermoplastic polymer-compatible organic liquid carrier. Such a carrier must be compatible with the thermoplastic

- polymer material of the thermoplastic moulding composition and is preferably also compatible with the other components to be included in the thermoplastic moulding composition of the invention. Typical carriers include hydrocarbons, hydrocarbon mixtures, alcohols, esters and mixtures of two or more thereof.
- 5 Preferably the thermoplastic polymer-compatible organic liquid carrier is an oil based vehicle. Examples of such vehicles of the materials available as Clearslip<sup>TM</sup> 2 and Clearslip<sup>TM</sup> 3 from ColorMatrix Europe Ltd., of Unit 9-11, Unity Grove, Knowsley Business Park, Knowsley, Merseyside, L34 9GT.
- 10 The thermoplastic polymer additive composition may also include one or more further functional additives. The sum of the amounts of said further additives preferably comprises less than 5wt%, preferably less than 2wt%, more preferably less than 1wt% of said additive composition.
- 15 The ratio of the weight of said acetaldehyde scavenger to the weight of hindered amine light stabiliser used in compositions referred to herein (e.g. used in the additive composition of the first aspect or in a dispersion, masterbatch or moulding composition) is suitably at least 1, preferably is at least 2, more preferably is at least 3 and, especially is at least 4. The ratio
- 20 may be less than 30, preferably less than 20, more preferably less than 10. Suitably, the ratio is in the range 2 to 10, preferably 3 to 8, more preferably 4 to 7.
- In a moulding composition, for example comprising PET described herein, the
- 25 amount of acetaldehyde scavenger in the composition may be in the range

0.01 to 2.0wt%, preferably in the range 0.01 to 0.2wt%, more preferably in the range 0.01 to 0.05wt%. The amount of hindered amine light stabiliser may be in the range 0.002 to 0.040wt%, preferably in the range 0.002 to 0.01wt%.

- 5 A mixture comprising acetaldehyde scavenger and hindered amine light stabiliser may be provided in a concentrated form, for example in the form of a masterbatch comprising solid material for mixing with a moulding composition or in the form of a solution or suspension. In such concentrated forms, the sum of the wt% of acetaldehyde scavengers and hindered amine light
- 10 stabilisers may be less than 50wt%, preferably less than 40wt% of the concentrated form; but preferably makes up at least 5wt% of the concentrated form. When a liquid dispersion is provided, the sum of the wt% of acetaldehyde scavengers and hindered amine light stabilisers in the dispersion may be in the range 20 to 50wt%, preferably 35 to 45wt%. In a solid
- 15 masterbatch, the sum of the wt% of acetaldehyde scavengers and hindered amine light stabilisers may be in the range 8 to 30wt%.

When compositions include more than one type of acetaldehyde scavenger and/or more than one type of hindered amine light stabiliser, ratios and/or wt%

20 referred to herein suitably refer to the sum of the amounts of scavengers and stabilisers as appropriate. Preferably, however, compositions include only a single type of acetaldehyde scavenger; and preferably include only a single type of hindered amine light scavenger.

In one embodiment, the amount of hindered amine light stabiliser used in the thermoplastic moulding composition of the invention is preferably less than 1000ppm, more preferably less than 500ppm, even more preferably less than about 250ppm, most preferably from about 10 to about 150ppm. For example, 5 the hindered amine light stabiliser may be added in an amount of from 10 to 100ppm of the thermoplastic moulding composition.

In one embodiment, the additive composition may be made by mixing the dry additive or additives in the form of a powder with a liquid organic carrier, 10 typically in a range of from about 1 to about 85 wt %, more usually in the range of from about 30 to about 50 wt %. The resulting additive composition comprising the hindered amine stabiliser and the acetaldehyde scavenger uniformly dissolved or dispersed in the liquid carrier can then be added to the thermoplastic polymer in ranges from about 0.0001% by weight to about 7% by 15 weight, for example, from 0.01% by weight up to about 5% by weight, based upon the weight of thermoplastic polymer component used.

It may not be desirable to use higher concentrations of the additive as this may interfere with the properties of the thermoplastic polymer material.

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In another aspect of the present invention there is provided a method of making a moulded article from a colourless or substantially colourless thermoplastic moulding composition which comprises:

- (a) providing a colourless or substantially colourless thermoplastic moulding 25 composition comprising polyethylene terephthalate;

- (b) admixing with the thermoplastic moulding composition at least one hindered amine light stabiliser and at least one acetaldehyde scavenger;
- (c) heating the colourless or substantially colourless thermoplastic moulding composition; and
- 5 (d) moulding the hot colourless or substantially colourless thermoplastic moulding composition so as to form a moulded article.

Typically the colourless or substantially colourless thermoplastic moulding composition is injection moulded to form a bottle preform and the resulting  
10 bottle preform is then blow moulded to form a bottle.

The invention further provides a method of making a blow moulded bottle from a polyethylene terephthalate moulding composition which comprises:

- (i) providing a colourless or substantially colourless polyethylene  
15 terephthalate moulding composition;
- (ii) admixing with the polyethylene terephthalate moulding composition at least one hindered amine light stabiliser and at least one acetaldehyde scavenger;
- (iii) heating the colourless or substantially colourless polyethylene  
20 terephthalate moulding composition;
- (iv) extruding the hot colourless or substantially colourless polyethylene terephthalate moulding composition so as to form a bottle preform; and
- (v) blow moulding the bottle preform at a blow moulding temperature so as to form a colourless or substantially colourless bottle;

Also provided in accordance with another aspect of the present invention is a method of making a useful article which comprises:

- (A) providing a colourless or substantially colourless thermoplastic moulding composition comprising polyethylene terephthalate;
- 5 (B) admixing with the thermoplastic moulding composition at least one hindered amine light stabiliser and at least one acetaldehyde scavenger;
- (C) forming a colourless or substantially colourless moulded article by a procedure including heating the colourless or substantially colourless thermoplastic moulding composition;
- 10 (D) after use of the moulded article, subjecting the material of the moulded article to recycling steps which include subjecting the material of the moulded article to elevated temperature conditions for a prolonged period of time; and
- (E) re-forming the thus treated material into a useful article.

15 Also provided in accordance with another aspect of the present invention is a method of making a useful article which comprises:

- (A) providing a colourless or substantially colourless thermoplastic moulding composition comprising polyethylene terephthalate and an acetaldehyde scavenger as an additive;
- 20 (B) forming a colourless or substantially colourless moulded article by a procedure including heating the colourless or substantially colourless thermoplastic moulding composition;
- (C) after use of the moulded article, admixing with the material of the moulded article at least one hindered amine light stabiliser;

(D) subjecting the resulting material of the moulded article to recycling steps which include subjecting the material of the moulded article to elevated temperature conditions for a prolonged period of time; and

(E) re-forming the thus treated material into a useful article.

5

In the re-forming step (E) typically techniques that can be used include moulding, extrusion, and other conventional processes for making articles of plastics materials, including bottles and fibres.

10 In such a method the colourless or substantially colourless thermoplastic (i.e. polyethylene terephthalate) moulding composition in step (B) can be injection moulded to form a bottle preform and then the resulting bottle preform can be blow moulded to form a bottle.

15 The invention further provides a method of making an article from a colourless or substantially colourless thermoplastic moulding composition that comprises:

(I) providing a colourless or substantially colourless thermoplastic moulding composition comprising recycled colourless or substantially colourless thermoplastic material, said recycled colourless or substantially colourless

20 thermoplastic material containing at least one acetaldehyde scavenger;

(II) admixing with the thermoplastic moulding composition an additive comprising a hindered amine light stabiliser; and

(III) extruding the resultant composition to form said article.

The article of step (III) may be a moulded article, such as a bottle preform, or a fibre or any other useful article, such as a tube, a crate, or the like.

Whilst a number of the aspects of the present invention utilise a moulding composition/polyethylene terephthalate which is preferably colourless or substantially colourless, a coloured moulding composition may also be used. Preferably, should a coloured moulding composition be used, it will be of a blue colour.

10 Polyethylene terephthalate is hygroscopic and after a period of approximately one year it is noticeable that preforms made of polyethylene terephthalate have taken up moisture from the air. Therefore, prior to the injection moulding process, polyethylene terephthalate granules for use in the invention are preferably dried for at least about 6 hours at from about 160°C to about 190°C,  
15 in a procedure that gives a slightly tactile product. The polyethylene terephthalate granules are transferred directly from the drier to the hopper of the injection-moulding machine. The hindered amine light stabiliser can then be added to and mixed with the thermoplastic polymer granules upon charging to the hopper. The injection moulding process typically occurs at between  
20 about 260°C and about 285°C, more preferably at about 270°C, and the thermoplastic polymer material has a dwell time within the machine of less than 1 minute. Once the preform has been blow moulded into an appropriate article, said article may be recycled by a suitable procedure which includes use of temperatures of up to about 300°C or greater and dwell times up to or in  
25 excess of 5 minutes, and sometimes for many hours.



The invention is further illustrated in the following examples with reference to the accompanying figures in which:

- 5    Figures 1 to 4 show specific examples of hindered amide light stabilisers; and  
     Figures 5 to 7 are plots of % transmission vs wavelength (in nm) for various  
     samples.

The following materials are referred to hereinafter:

10

Anthranilamide – an acetaldehyde scavenging agent;

VORIDIAN 9921 w – a copolymer PET obtained from Eastman Chemical  
Company;

- CHIMASSORB 944 – an oligomeric hindered amine light stabiliser of molecular  
15    weight (Mn) 2000-3000 obtained from Ciba Speciality Chemicals (Compound  
     VII in Figure 2);

CYASORB UV-3346 – a hindered amine light stabiliser of molecular weight  
about 1600 obtained from Cytec Industries Inc (compound XIII in Figure 3);

CLEARTUF P82 – a polyethylene terephthalate obtained from M&G Group.

- 20    Voridian AA reducer – an acetaldehyde reducing formulation from Viridian  
     (referred to as Voridian LAAC) containing low molecular weight polyamide;

Tinuvin 622 LD – a powdered oligomeric hindered amine light stabiliser of  
molecular weight (Mn) 3100-4000 obtained from Ciba Speciality Chemicals  
(Compound IV in Figure 1);

- 25    MXD6 – a polyamide obtained from Mitsubishi Chemical Company;

HALS – refers to “hindered amine light stabiliser(s)”.

Example 1

5 Anthranilamide acetaldehyde scavenging agent and CHIMASSORB 944 were incorporated at levels detailed in Table 1 into VORIDIAN 9921w polyethylene terephthalate (PET) resin which was moulded into a 35g weight bottle blowing preform using a HUSKY injecting moulding machine. The preform was then transferred to a bottle-blowing machine, reheated by an infrared lamp and  
10 stretch blown into a 1litre bottle.

The blown bottle was then ground to fragments and washed with hot water, to simulate the recycle process. After washing the fragments of simulated recycled PET were dried by heating them at approximately 160°C for five (5)  
15 hours and were then extruded at 270°C using a laboratory extrusion rig and cut into granules.

The experimental recycled PET granules were then crystallised by holding at 180°C for six (6) hours and then transferred to a batchwise rotation vacuum  
20 solid state polymerisation machine. During the Solid State Polymerisation (SSP) process the recycled PET granulate was first subjected to a temperature of 220°C for sixteen (16) hours and then allowed to cool to below a temperature of 170°C.

The simulated recycled PET granulate was then injection moulded into 2.5mm thick plaque using a BOY 22M injecting moulding machine in order to prepare samples for optical analysis.

- 5 The % light transmission at the wavelengths 450 nm and 550 nm was determined using a MINOLTA Spectrophotometer CM-3700d and results are provided in Table 2.

Table 1

| Example No | PET            | Acetaldehyde Scavenger |                                     | HALS            |                                     |
|------------|----------------|------------------------|-------------------------------------|-----------------|-------------------------------------|
|            | Identity       | Identity               | Amount based on weight of PET (wt%) | Identity        | Amount based on weight of PET (wt%) |
| 1          | VORIDIAN 992lw | Anthranilamide         | 0.033                               | CHIMASSORB 944  | 0.006                               |
| C1         | VORIDIAN 992lw | Anthranilamide         | 0.033                               | -               | -                                   |
| 2          | VORIDIAN 992lw | Anthranilamide         | 0.033                               | CYASORB UV-3346 | 0.006                               |
| 3          | Cleartuf P82   | Anthranilamide         | 0.033                               | CHIMASSORB 944  | 0.006                               |
| C2         | Cleartuf P82   | -                      | -                                   | -               | -                                   |
| C3         | Cleartuf P82   | Anthranilamide         | 0.033                               | -               | -                                   |

Example C1

The procedure of Example 1 was generally followed except that the  
5 CHIMASSORB 944 was omitted as summarised in Table 1. The % light  
transmission at the wavelengths 450nm and 550nm was determined in the  
manner described in Example 1 for a plaque prior to the simulated recycle  
process of Example 1 and also after the simulated recycle process. Results  
are summarised in Table 2.

10

Table 2

| Composition<br>Examined<br>(Example No) | Time of<br>Examination                | % TRANSMISSION |        |
|---|---------------------------------------|----------------|--------|
|   |                                       | @ 450nm        | @550nm |
| 1                                       | After simulated<br>recycle process    | 74             | 81     |
| C1                                      | Prior to simulated<br>recycle process | 79             | 84     |
| C1                                      | After simulated<br>recycle process    | 71             | 79     |

The increased use of the acetaldehyde reducing agent anthranilamide in PET  
used to blow bottles has been found to cause a reduction in the light  
15 transmission and an increase in the yellow tint of PET when the bottles are

recycled. The addition of Chimassorb 944 (Hindered Amine Light Stabiliser) in addition to the anthranilamide significantly reduces the loss of transparency.

#### Example 2

5

By a process analogous to Example 1, CYASORB UV-3346 was incorporated in an anthranilamide/PET formulation as detailed in Table 1. Results showed that the CYASORB had a similar effect to the HALS of Example 1.

#### 10 Example 3 and Comparative Examples C2 and C3

In this example the acetaldehyde reducing properties of HALS in conjunction with conventional acetaldehyde reducers/scavengers was demonstrated.

15 Preparation of Experimental Samples - Three parallel experiments were carried out. The experimental procedure varied only in the number and level of acetaldehyde reducer/scavenger and HALS agents added to the commercial PET, Cleartuf P82, as detailed in Table 1.

20 In the examples, Cleartuf P82 polyethylene terephthalate was loaded into a commercial injection-moulding machine (Netstal HP3500) and any additives were incorporated. Each mixer charge was injection moulded into a 47g weight bottle blowing preforms. Samples were taken from each of the experimental preforms and set aside for individual examination for  
25 acetaldehyde content, in the manner described below.

Acetaldehyde Analysis - Each sample was immersed in liquid nitrogen and subsequently ground down by Retsch grinder to a particle size less than 1mm and subjected to chromatographic analysis for free acetaldehyde concentration using a Perkin Elmer XL gas chromatograph with FID detector. Pure acetaldehyde (99.5%) was obtained from Sigma Aldrich for calibration purposes.

Results of the analyses for Examples 3, C2 and C3 are provided in Table 3 which show that the addition of CHIMASSORB 944 (Hindered Amine Light Stabiliser) in addition to anthranilamide (acetaldehyde reducing agent) to PET prior to injection moulding the PET causes an unexpected further lowering of acetaldehyde level in the injection moulded article (bottle pre-form) relative to the anthranilamide alone (28% reduction).

15

Table 3

| Example No | COMPOSITION EXAMINED                                    | ACETALDEHYDE LEVEL (ppm) | % REDUCTION |
|------------|---|--------------------------|-------------|
| C2         | PET (Cleartuf P82)<br>with no additives                 | 6.9                      |             |
| C3         | PET (Cleartuf P82)<br>with 0.033% active Anthranilamide | 3.9                      | 43          |

|   |   |     |      |
|---|---|-----|------|
| 3 | PET with 0.033%<br>active<br>Anthranilamide+<br>0.0060%<br>Chimassorb 944 | 2.8 | 59.1 |
|---|---|-----|------|

Examples 4 to 6 and C4.1, C4.2 and C4.3

PET was predried and mixed with additives (acetaldehyde scavengers and/or  
5 HALS) and the material extruded using a Mapex 20mm extruder. After  
extrusion, the material was pelletized and then subjected to Acetaldehyde  
Analysis in the manner described above. The pellets were then further  
crystallised, dried and re-extruded again using the Mapex extruder. Pellets  
produced were then crystallised, dried and subjected to solid state  
10 polymerisation. Thereafter, 2.5mm plaques were prepared as described with  
reference to Example 1. Details on the compositions and the acetaldehyde %  
reduction are provided in Table 4.

Table 4

| Example<br>No | Acetaldehyde<br>Scavenger |                       | HALS              |                       | Acetaldehyde<br>% reduction |
|---------------|---------------------------|-----------------------|-------------------|-----------------------|-----------------------------|
|               | Identity                  | Amount<br>used<br>wt% | Identity          | Amount<br>used<br>wt% |                             |
| C4.1          | -                         | -                     | -                 | -                     | 0                           |
| C4.2          | Anthranilamide            | 0.0330                | -                 | -                     | 47.4                        |
| 5             | Anthranilamide            | 0.0330                | Tinuvin 622       | 0.0060                | 70.4                        |
| C4.3          | Voridian AA<br>reducer    | 0.1500                | -                 | -                     | 58.4                        |
| 6             | Voridian AA<br>reducer    | 0.1500                | CHIMASSORB<br>944 | 0.0060                | 65.2                        |

Examples 7, C5 and C6

- 5 By processes analogous to the process described for Example 4 etc, colour spectrum data was determined for the compositions detailed in Table 5, after the simulated recycle process using a Minolta Spectrophometer CM-3700D. Colour spectrum data and % transmission at 450nm and 550nm are provided in Table 6 and the % light transmission over the wavelengths 400 to 700nm is
- 10 represented graphically in Figure 5.



Table 5

| <u>Example No</u> | <u>Acetaldehyde Scavenger</u> |  | <u>HALS</u>        |  |
|-------------------|-------------------------------|--|--------------------|--|
|                   | Identity                      | Amount<br>based on<br>weight of<br>PET (wt%) | Identity           | Amount<br>based on<br>weight of<br>PET (wt%) |
| 7                 | Anthranilamide                | 0.0330                                       | CYASORB<br>UV-3346 | 0.0060                                       |
| C5                | -                             | -  | -                  | -  |
| C6                | Anthranilamide                | -  | -                  | -  |

5

Table 6

| Example<br>No | Colour Spectrum data |          |          |          |          | % Transmission |        |
|---------------|----------------------|----------|----------|----------|----------|----------------|--------|
|               | L*                   | a*       | b*       | C*       | h°       | 450nm          | 550nm  |
| 7             | 91.90008             | -1.25264 | 8.44944  | 8.5418   | 98.43264 | 71.146         | 80.836 |
| C5            | 93.6646              | -0.6909  | 2.61336  | 2.70318  | 104.8108 | 81.968         | 84.37  |
| C6            | 91.37288             | -1.19754 | 10.77664 | 10.84302 | 96.34708 | 67.288         | 79.822 |

Referring to Figure 1, it will be noted that for all wavelengths between 400 to about 600nm, the material of Example 7 transmits more light than for comparative Example C6 which does not include any HALS. As a result,

10 bottles (or the like) made from the material of Example 7 will appear clear and/or less coloured than bottles made out of the material of Example C6.

Also, the % acetaldehyde reduction was assessed for Example 7 and found to be 54.7% which shows that the material of Example 7 reduces both acetaldehyde and improves light transmission.

5

Examples 8, 9, C7 and C8

By processes analogous to the process described for Example 4 etc, transmission data was obtained for the compositions detailed in Table 7, after  
10 the simulated recycle process, using the Minolta Spectrophometer referred to previously. Results are represented graphically in Figure 6 (Example 8 and C7) and Figure 7 (Example 9 and C8).

Table 7

| Example<br>No | Acetaldehyde Scavenger                 |  | HALS              |  |
|---------------|--|--|-------------------|--|
|               | Identity                               | Amount<br>based on<br>weight of<br>PET (ppm) | Identity          | Amount<br>based on<br>weight of<br>PET (ppm) |
| 8             | Anthranilamide                         | 500  | CHIMASSORB<br>944 | 100  |
| C7            | Anthranilamide                         | 500  | -                 | -  |
| 9             | 1,6-bis (2-aminobenzamidoyl<br>hexane) | 500  | CHIMASSORB<br>944 | 100  |
| C8            | 1,6-bis (2-aminobenzamidoyl<br>hexane) | 500  | -                 | -  |

Referring to Figures 6 and 7, it will be noted that, in both cases, the addition of

5 HALS resulted in a material which transmitted more light compared to corresponding materials in the absence of the HALS.

Example C9

Plaques were prepared as described with reference to Example 4 etc, using  
5 PET and CHIMASSORB 944 HALS (0.006% on weight of PET) in the absence  
of any acetaldehyde scavenger. In an acetaldehyde analysis, no improvement  
in the acetaldehyde level was observed using the HALS alone.

Example 10 and C10

10

Plaques were prepared as described for Example 4 etc. from Voridian 9221w  
and the materials referenced in Table 8. The b\* values were measured, as  
shown in the table. It will be noted that the addition of the HALS improves the  
colour of the plaque.

Table 8

| Example No | Acetaldehyde Scavenger |                                       | HALS           |                                       | b*       |
|------------|------------------------|---------------------------------------|----------------|---------------------------------------|----------|
|            | Identity               | Amount based on weight of PET ppm wt% | Identity       | Amount based on weight of PET ppm wt% |          |
| 10         | MXD6                   | 0.15                                  | CHIMASSORB 944 | 0.006                                 | 6.276125 |
| C10        | MXD6                   | 0.15                                  | -              | -                                     | 7.077025 |

Discussion

5

The results show that the addition of a HALS to a PET and acetaldehyde scavenger composition leads to a surprising improvement in the light transmission of the material after a simulated recycle process (see Table 2) (and compare Example 1 and C1 after a simulated recycle process; also

10 compare Example 7 with Examples C5 and C6 and Figure 4 to 6). The improvement in transmission is clearly shown in the figures. Also, Example 7 shows both an improvement in the transmission and a reduction in acetaldehyde content.

The ability to improve transmission and/or transmission allows more flexibility in toning options, especially the use of blue toning.

Furthermore, the addition of a HALS alone was found to provide no  
5 improvement in the reduction of acetaldehyde content of a PET when added to the PET alone (see Example C9). The addition of an acetaldehyde scavenger alone provides a clear reduction in the acetaldehyde content of a PET after a simulated recycle process (compare Examples 3 and C2 and C3. The inclusion of a HALS in a composition comprising PET and acetaldehyde  
10 scavenger appears to act synergistically with the acetaldehyde scavenger resulting in a surprising reduction in the acetaldehyde content of a PET after a simulated recycle (compare Examples C3 and 3).